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The Crystal Structure of cis-2-acetamido-3-fluoronorbornane

by

Neal M. Ely

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TECHNICAL REPORT FJSRL-TR-81-0006

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Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
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The X-ray crystal structure of cis-2-acetamido-3-fluoronorbornane (formed during the photolysis of norbornene and XeF_2 in acetonitrile) is reported.

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SUMMARY

The X-ray crystal structure of cis-2-acetamido-3-fluoronorbornane (formed during the photolysis of norbornene and XeF_2 in acetonitrile) is reported.

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INTRODUCTION

Extensive work has been carried out at the Seiler Laboratory to elucidate the nature of the light initiated reaction between XeF_2 and norbornene in acetonitrile. Six major products can be isolated from this reaction, including three which result from reaction with solvent molecules[1]. While the molecular composition of these compounds was clearly identified, the exact stereochemistry was not absolutely determined. To unambiguously ascertain this, an x-ray crystal structure of the compound tentatively identified as the cis (or exo-exo) fluoroamide compound was performed. This work was contracted out and accomplished by the Molecular Structure Corporation, College Station, Texas.

EXPERIMENTAL

Data Collection

A colorless needlelike crystal of the compound, having approximate dimensions of 0.08 x 0.08 x 0.20 mm was mounted in a glass capillary with its long axis roughly parallel to the phi axis of the goniometer. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 A) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 24 reflections in the range $7 < \theta < 20°$, measured using the computer controlled diagonal slit method of centering. The Monoclinic cell parameters and calculated volume are: a = 10.641(2), b = 9.542(2), c = 18.979(4) A, β = 106.48(2), °, V = 1847.9A^3. For Z = 8 and F.W. = 171.22 the calculated density is 1.23 g/cm^3. As a check on crystal quality, omega scans

of several intense reflections were measured the width at half-height was 0.30° with a take-off angle of 2.8°, indicating good crystal quality. From the systematic absences of:

$$0k0 \quad k=2n+1$$

$$h01 \quad l=2n+1$$

and from subsequent least-squares refinement, the space group was determined to be P2-1/c (# 14).

The data were collected at a temperature of 23 ± 1° using the w-θ scan technique. The scan rate varied from 2 to 20 °/min (in omega). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 120.0°. The scan range (in deg.) was determined as a function of θ to correct for the separation of the Kα doublet[2] ; the scan width was calculated as follows:

$$\theta \text{ scan width} = w \text{ scan width} = 0.6 + 0.300 \tan \theta$$

Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 3.7 mm; the vertical aperture was set at 2.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 15.5.

Data Reduction

A total of 3003 reflections were collected, of which 2736 were unique and not systematically absent. As a check on crystal and electronic

stability 3 representative reflections were measured every 41 min. The slope of the least-squares line through a plot of intensity versus time was -35 ± 14 counts/hour which corresponds to a total loss in intensity of 2.3%. A linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.024 with an average of 1.012.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 7.9 cm-1 for Cu Kα radiation. No absorption correction was made. An extinction correction was not necessary.

Structure Solution and Refinement

The structure was solved by direct methods. Using 186 reflections (minimum E of 1.36) and 4409 relationships, a total of 32 phase sets were produced. All 24 non-hydrogen atoms were located from an E-map prepared from the phase set with probability statistics: absolute figure of merit = 1.06, residual = 0.18, and psi zero = 1.340. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|Fo| - |Fc|)^2$ and the weight w is defined as $4Fo^2/\sigma^2\ (Fo^2)$.

The standard deviation on intensities, (Fo^2), is defined as follows

$$\sigma^2(Fo^2) = [\ S^2\ (\ C + R^2B\ ) + (\ pFo^2)^2\ ]\ /\ Lp^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz-polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.070.

Scattering factors were taken from Cromer and Waber[3]. Anomalous dispersion effects were included in Fc[4]; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer[5]. Only the 346 reflections having intensities greater

than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 97 variable parameters and converged (largest parameter shift was 0.1 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; ||Fo| - |Fc||/\Sigma|Fo| = 0.158$$

$$R2 = \text{SQRT}\ (\Sigma w(|Fo| - |Fc|)^2/\Sigma w\ Fo^2) = 0.194$$

The standard deviation of an observation of unit weight was 4.13. The highest peak in the final difference Fourier had a height of 0.21 e/A^3 with an estimated error based on ΔF^6 of 0.05. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends.

Since the crystal was quite small and diffracted rather poorly, the data was of less than desirable quality. Many crystals were examined and no better crystal was found. Although there is no doubt as to the basic structure, the poor quality of the data evidences itself in the high standard deviations of individual bond distances and angles and the somewhat anomalous isotropic temperature factors observed for some atoms.

All calculations were performed on linked PDP-11/45-11/60 computers using the Enraf-Nonius Structure Determination Package[7] as well as private programs of Molecular Structure Corporation[8].

TABLE I

Crystal Data

C9 H14 F N O

F.W. 171.22 F(000) = 736

Crystal dimensions: 0.08 x 0.08 x 0.20 mm

Peak width at half-height = 0.30°

Cu Kα radiation (λ = 1.54184 A)

Temperature = 23 ± 1°

Monoclinic space group P2-1/c

a = 10.641 (2) A b = 9.542 (2) A c = 18.979 (4) A

β = 106.48 (2)°

$V = 1847.9\ A^3$

$Z = 8 \quad \rho = 1.23\ g/cm^3$

μ = 7.9 cm-1

TABLE II

Intensity Measurements

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Ni foil, factor 15.5
Take-off angle:	2.8°
Detector aperture:	2.0 to 3.7 mm horizontal
	2.0 mm vertical
Crystal-to-detector distance:	21 cm
Scan type:	w-θ
Scan rate:	2 - 20°/min (in omega)
Scan width, deg:	0.6 + 0.300 tan θ
Maximum 2θ:	120.0°
No. of reflections measured:	3003 total, 2736 unique
Corrections:	Lorentz-polarization
	Linear decay (from 1.000 to 1.024 on I)

TABLE III

Structure Solution and Refinement

Solution:	Direct methods
Hydrogen atoms:	Not included
Refinement:	Full-matrix least-squares
Minimization function:	$\Sigma w(\|Fo\|-\|Fc\|)^2$
Least-squares weights:	$4Fo^2/\sigma^2(Fo^2)$
"Ignorance" factor:	0.070
Anomalous dispersion:	All non-hydrogen atoms
Reflections included:	346 with $Fo^2>3.0\sigma(Fo^2)$
Parameters refined:	97
Unweighted agreement factor:	0.158
Weighted agreement factor:	0.194
Esd of observation of unit weight:	4.13
Convergence, largest shift:	0.1σ
Highest peak in final difference Fourier:	0.21 (5) e/A^3
Computer hardware:	Linked PDP-11/45-11/60
Computer software:	Enraf-Nonius SDP and private prgrams of Molecular Structure Corporation

TABLE IV

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
F1	C4	1.43(4)	C5	C9	1.69(4)	C12	C13	1.52(3)
O1	C2	1.37(4)	C6	C7	1.76(3)	C12	C16	1.59(3)
N1	C2	1.44(3)	C7	C8	1.71(3)	C13	C14	1.49(3)
N1	C3	1.50(2)	C8	C9	1.60(3)	C14	C15	1.50(3)
C1	C2	1.31(3)	F2	C13	1.66(2)	C14	C18	1.63(3)
C3	C4	1.49(4)	O2	C11	1.23(4)	C15	C16	1.58(3)
C3	C7	1.49(3)	N2	C11	1.50(3)	C16	C17	1.71(3)
C4	C5	1.51(4)	N2	C12	1.52(2)	C17	C18	1.66(3)
C5	C6	1.45(3)	C10	C11	1.48(3)			

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Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE V

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	N1	C3	131.(3)	C5	C6	C7	103.(2)
O1	C2	N1	103.(3)	C3	C7	C6	94.(2)
O1	C2	C1	126.(4)	C3	C7	C8	96.(2)
N1	C2	C1	128.(4)	C6	C7	C8	81.(2)
N1	C3	C4	122.(3)	C7	C8	C9	119.(3)
N1	C3	C7	99.(2)	C5	C9	C8	91.(2)
C4	C3	C7	115.(3)	C11	N2	C12	124.(2)
F1	C4	C3	107.(3)	O2	C11	N2	105.(3)
F1	C4	C5	97.(3)	O2	C11	C10	142.(4)
C3	C4	C5	105.(3)	N2	C11	C10	111.(3)
C4	C5	C6	108.(3)	N2	C12	C13	118.(2)
C4	C5	C9	89.(3)	N2	C12	C16	107.(2)
C6	C5	C9	107.(3)	C13	C12	C16	103.(2)

Atom 1	Atom 2	Atom 3	Angle
F2	C13	C12	105.(2)
F2	C13	C14	95.(2)
C12	C13	C14	107.(2)
C13	C14	C15	108.(2)
C13	C14	C18	89.(2)
C15	C14	C18	112.(2)
C14	C15	C16	98.(2)
C12	C16	C15	101.(2)
C12	C16	C17	93.(2)
C15	C16	C17	98.(2)
C16	C17	C18	108.(2)
C14	C18	C17	95.(2)

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Numbers in parentheses are estimated standard deviations in the least significant digits.

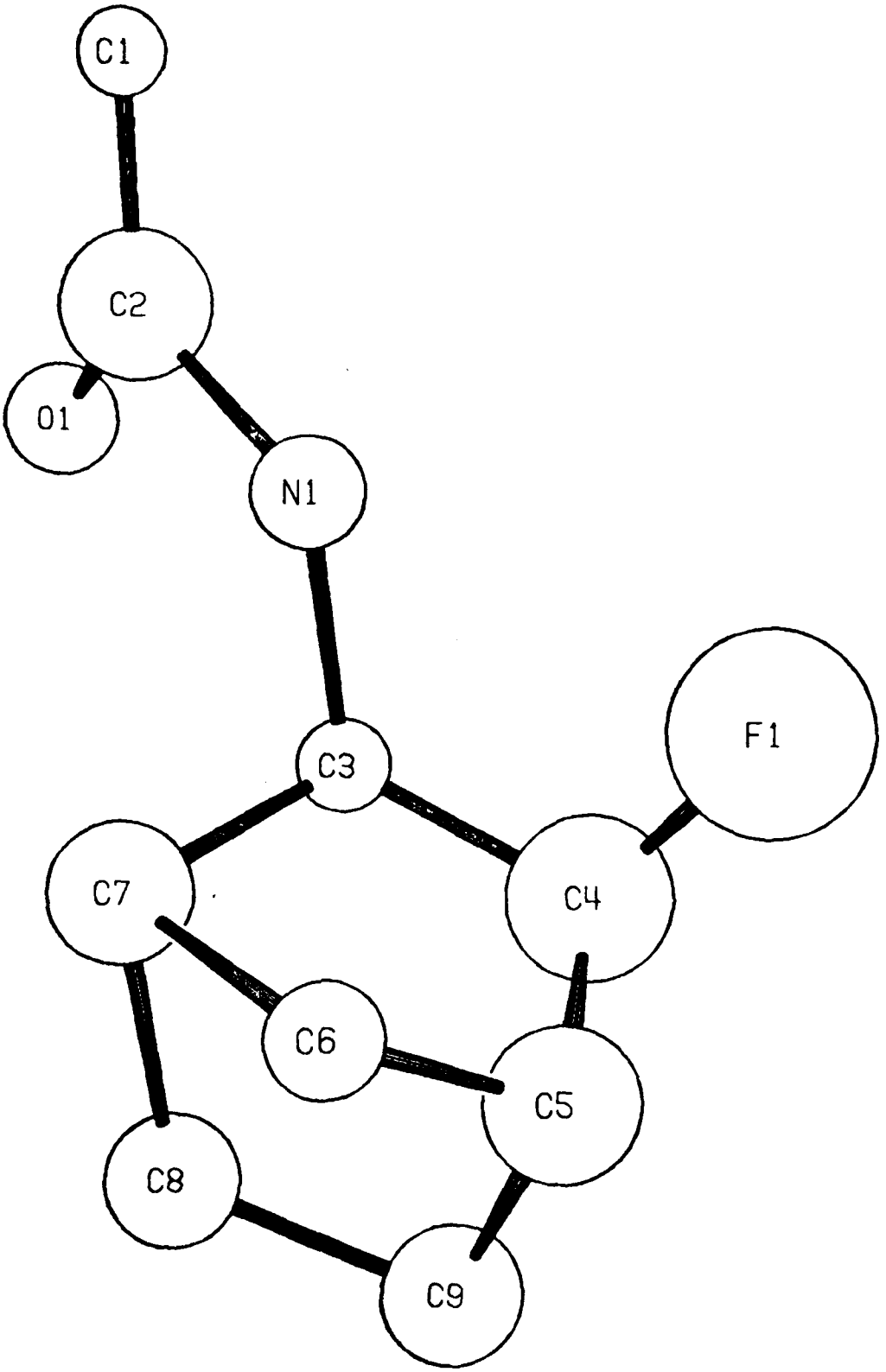

FIGURE 1

RESULTS

Although the diffraction data were less than optimum, the stereochemistry of the molecule was clearly ascertained. A stereoview of the molecule showing 20% probability ellipsoids is shown in Figure 1. The compound is indeed the exo - exo isomer as we had postulated.

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(8) Additional experimental data such as least-squares planes and intensity data for reflections is available at FJSRL.

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